



## Facilitated transport of cadmium by bulk liquid membrane using Aliquat 336 as carrier: separation from other heavy metal ions

Nasser Dalali\*, Hadi Habibi

*Faculty of Science, Phase Separation and FIA Laboratory, Department of Chemistry, University of Zanjan, Zanjan, Iran, email: Nasser\_zn@yahoo.com (N. Dalali)*

Received 21 May 2014; Accepted 16 July 2014

### ABSTRACT

Efficient transport of cadmium ions from chloride solutions through a bulk liquid membrane was studied at 25°C using Aliquat 336 in chloroform as carrier solution. The influence of different parameters, including chloride concentration in the feed solution, reagent concentration and type of organic solvent in the membrane phase, and type of stripping solution as the receiving phase was investigated. The transport yield of cadmium ions from a 0.05 mol L<sup>-1</sup> sodium chloride solution (pH = 6) through a chloroform solution of Aliquat 336 (0.025 mol L<sup>-1</sup>) into the receiving phase (distilled water) was found to be 93 (±1.3) % after 3 h. The efficiency and selectivity of the method were investigated by competitive experiments on the mixture of Cd<sup>2+</sup> with Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup> and Zn<sup>2+</sup> ions. The accessibility of the method was tested for recovery of Cd from Ni–Cd cake (zinc plant purification cake), spent Ni–Cd cells and wastewater samples.

*Keywords:* Cadmium separation; Bulk liquid membrane; Wastewater; Aliquat 336

### 1. Introduction

Cadmium is generally associated with zinc and its compounds; it is recovered as a by-product of the smelting of zinc and lead–zinc ores [1,2]. So zinc processing plant is considered as a primary source for cadmium. The element has found vast applications in different industries such as pigments, electroplating, metallurgical products, chemicals and plastics, which account for nearly one-fourth of its consumption. Rechargeable Ni–Cd batteries account for three-fourth of the cadmium consumed, hence, to be considered as secondary cadmium source. Despite its useful and vast applications, cadmium is known to be toxic element which tends to be concentrated in environmental

systems and humans; it can cause dysfunction of the kidneys, liver and lungs [3,4]. Most often, cadmium could enter the water system through industrial discharge, thus, its removal and/or recovery from the various effluents have attracted much attention either from the scientific and technological or environmental and economical points of view. According to the literature, there are two major methods to reach cadmium metal. If the material being treated (from any of such sources) consists of Cd, Zn, Cu, Pb and other elements (at trace concentrations), selectively leaching of this material with sulphuric acid will precipitate Cu and Pb and filtration will give a solution of Cd and Zn sulphates. Then, cementation with zinc powder will give spongy cadmium which can be melted with addition of soda to remove any co-precipitated zinc or re-leached to be electrowon.

\*Corresponding author.

But if the beginning material consists of Cd associated with Ni, Co and Zn, the above-mentioned conventional method cannot be used to separate Cd, because Ni and Co; too will be dissolved together with Cd and Zn and cementation will precipitate Ni and Co along with Cd, giving an impure sponge [5]. The leaching of nickel and cobalt in chloride media has been applied for many years at Falconbridge's nickel plant in Norway [6]. However, purification of metal from such leach solutions can be difficult. Solvent extraction could separate cobalt and nickel from high concentrated chloride solutions, due to the more stable chloride complex formation by cobalt than nickel [7].

Removal of cadmium is more difficult because of mixed chloride complex formation. Cadmium extraction along with zinc from chloride and thiocyanate media has been reported by Wassink et al. [8]. Most of the reports on selective extraction/separation of Cd from Zn are based upon the application of synergic effects. Jia et al. have used the mixture of primary amine N1923 and organophosphorus acid Cyanex301 for this purpose [9].

Solvent extraction separation of Cd(II) and Zn(II), with di-(2-ethylhexyl)-phosphoric acid (D<sub>2</sub>EHPA), and an aqueous hexadentate ligand with nitrogen donors, N,N,N',N'-(tetrakis-2-pyridylmethyl) ethylenediamine (TPEN) was studied by Takeshita et al., where TPEN acted as a synergist for the extraction of Cd(II) and a masking agent for that of Zn(II) [10]. They also have reported the same process using Cyanex301 and TPEN [11].

Many metal ions including cadmium form anionic chloro complexes in chloride medium, which can be extracted by protonated amines, for which acidic conditions are required [12]. Quaternary ammonium salts behave like protonated amines, in a wide pH range. Moreover, quaternary ammonium salts extract cadmium from chloride solution more strongly than protonated amines, as  $MCl_4^{2-}$  complexes [8,13].

The use of liquid membranes containing specific metal ion carriers offers an alternative to the solvent extraction processes for selective separation and concentration of the metal ions from aqueous solutions. Facilitated transport by liquid membranes is a known technique for separation of metal ions [14]. The advantages of this technique include; low cost and energy consumption. Several investigations on the separation of cadmium by liquid membranes are based on the anionic complexes of this metal ion. He et al. have used amine extractants [15], Wang et al. have used Aliquat 336/PVC membrane [16], Alguacil et al. have reported the cadmium transport using Cyanex921 and 923 [17], Yaftian et al. have used

hexadecyltrimethylammonium bromide for transport of cadmium from iodide media [18].

The transport of Cd (II) through the supported liquid membrane has been reported by Juang et al. [19], where both the feed and receiving phases contained HCl (0.1 and 0.01 mol L<sup>-1</sup>, respectively). This procedure is very slow and the HCl concentration in the receiving phase is crucial and a limiting parameter, which limits the applicability of the technique. Although iodide is not a suitable media for industrial application Kumbasar has reported the emulsion liquid membrane transport of Cd(II) via Aliquat 336, and Amberlite LA-2 into the ammonia solution [20, 21]. We recently reported the transport/separation of Cd(II) and Zn(II) as chloro complexes with the aid of the same membrane (Aliquat 336 solution in benzene) using ammonia and/or ethylene diamine tetraacetic acid (EDTA) as the receiving phase with a good efficiency and selectivity [22].

In continuation to that the present work was an attempt to systematically explore the application of Aliquat 336 diluted with aliphatic solvents, in the more convenient and milder conditions (i.e. to use a neutral feed phase, and an easily available, cost effective and neutral stripping solution like distilled water as the receiving phase), and also the effect of Cl<sup>-</sup> concentration on selectivity for extraction of cadmium. Hence, the major difference with our previous work is the use of: (i) almost neutral feed solution, (ii) replacement of Benzene (toxic solvent) with a less-toxic aliphatic solvent as diluent and (iii) distilled water as receiving phase.

The selectivity of method was evaluated by extracting cadmium ions from its mixtures with some diverse coexisting metal ions including cobalt, nickel and specially zinc by varying the Cl<sup>-</sup> concentration. Later, the accessibility of the method was investigated by application to removal of cadmium from leach solutions of zinc plant purification cake and spent Ni–Cd cells. Finally, a mechanism was suggested for cadmium transport different from our previous report [22].

## 2. Material and methods

### 2.1. Chemicals and reagents

All chemicals and reagents were of highest available purity, and all aqueous solutions were prepared in doubly distilled deionized water. Aliquat 336 was supplied by Henkel; nitric acid (65%), hydrochloric acid (32%) and sulphuric acid (96%) with general reagent grade were obtained from Merck (Darmstadt, Germany), sodium chloride, sodium hydroxide, ethylene diamine, ammonia and EDTA were analytical reagent grade

(Merck). The solvents chloroform, dichloromethane, 1,2-dichloroethane and carbon tetrachloride were obtained from Merck. Metal salts (mainly chloride) were purchased from Fluka and used for preparation of stock solutions ( $1,000 \text{ mg L}^{-1}$ ). Working solutions were prepared by appropriate dilution of the stock solutions. Diluted hydrochloric acid and sodium hydroxide solutions were used for pH adjustment.

## 2.2. Apparatus

A Varian Model spectrAA220 atomic absorption spectrometer (Mulgrave, Victoria, Australia) equipped with deuterium lamp background corrector was used for metal analysis. A circulating thermostatic water bath (JULABO MP5) was used for temperature control during the experiments. Magnetic stirrer (model MR3001 K) Heidolph was used for agitation of the phases. The pH measurements were accomplished with a Metrohm model 692 pH/ion meter equipped with a combined glass–calomel electrode.

## 2.3. Sample preparation

The zinc plant cadmium cake was obtained from Calcimine Co., Dandy zinc industrial region, Zanjan-Iran. The cake sample was crashed, grinded and dried at  $110^\circ\text{C}$  for 2 h. After cooling the sample to room temperature, 2.5 g was taken in three replicates, leached in  $100 \text{ mL HCl } 2 \text{ mol L}^{-1}$  at  $100^\circ\text{C}$  for 1 h. This sample contains about 20% Zn, 9% Cd, 4% Ni and minor amounts of iron. The majority of Zn, Ni and Fe were precipitated using different reagents and pH adjustment.  $10 \text{ mL}$  of this solution was diluted to  $1,000 \text{ mL}$  with distilled water and after addition of NaCl and pH adjustment it was subjected to the transport (this solution contains  $23 \text{ mg L}^{-1} \text{ Cd(II)}$ ,  $45 \text{ mg L}^{-1} \text{ Zn(II)}$ ,  $8 \text{ mg L}^{-1} \text{ Ni(II)}$  and  $2 \text{ mg L}^{-1} \text{ Co(II)}$ ). An industrial wastewater prior to treatment collected from zinc processing plant was filtered to remove any particulate matter and performed the extraction process within 48 h.

Spent Ni–Cd cells (Sony) were crashed out, then three replicate samples of the dried material ( $2.0 \text{ g}$ ) were leached with  $20 \text{ mL}$  of  $\text{H}_2\text{SO}_4 \text{ } 3 \text{ mol L}^{-1}$  for 4 h at  $80^\circ\text{C}$ . The resulted leach liquor contains average of  $6,744.6$ ,  $1,178.6$  and  $13,498.7 \text{ mg L}^{-1} \text{ Cd(II)}$ ,  $\text{Co(II)}$  and  $\text{Ni(II)}$ , respectively. This solution was diluted 100 times with distilled water, adjusted to desired chloride concentration and pH.

## 2.4. Experimental method

A glass cylindrical cell (i.d.  $4.5 \text{ cm}$ ) holding a glass tube (i.d.  $2.25 \text{ cm}$ ) which separates the source and

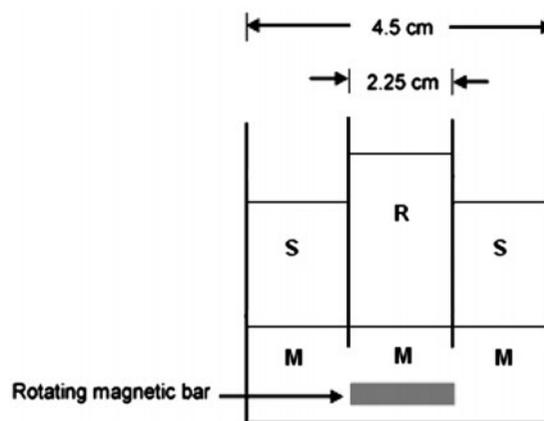


Fig. 1. Experimental set-up for the transport experiments: (S) feed phase,  $10 \text{ mL}$ ; (M) liquid membrane,  $20 \text{ mL}$ ; (R) receiving phase,  $10 \text{ mL}$ .

receiving aqueous phases was used for the transport experiments (Fig. 1).

The cell was placed in a thermostatic water bath to maintain the temperature at  $25^\circ\text{C}$ . The feed phase (S) was  $10\text{-ml}$  aqueous solution of Cd ( $25 \text{ mg L}^{-1}$ ), containing  $\text{NaCl } 0.05 \text{ mol L}^{-1}$  having pH 6–7.  $10 \text{ mL}$  distilled water was used as receiving phase (R).  $20 \text{ mL}$  solution of Aliquat 336 ( $0.025 \text{ mol L}^{-1}$ ) in chloroform (M) was laid below these aqueous phases and bridged the two phases. The organic layer (M) was stirred by Teflon-coated magnetic bar at  $150 \text{ rpm}$ . The metal content was measured by taking  $3 \text{ mL}$  from each aqueous phase and analysing it by flame atomic absorption spectrometry.

## 3. Results and discussion

### 3.1. Effect of chloride concentration in the feed phase

Cadmium can be found as  $\text{CdCl}_3^-$  and  $\text{CdCl}_4^{2-}$  complexes in aqueous chloride solutions, and Aliquat 336 could extract them into an organic phase by forming an ion pair with such complexes. Therefore, the influence of chloride concentration on the efficiency of cadmium transport was investigated in the range of  $0\text{--}0.8 \text{ mol L}^{-1}$ . Fig. 2(a) shows that cadmium concentration in the receiving phase increases rapidly with increase in the concentration up to  $0.05 \text{ mol L}^{-1}$  chloride and it decreases with almost the same rate in the feed phase (Fig. 2(b)). While the extraction efficiency of zinc, cobalt and nickel is much less in this concentration range (i.e. 11, 0.2 and 0.07% at the most), respectively, and much of them remain in the feed phase; which can be attributed to the different stability constants of their chloro complexes. The result is

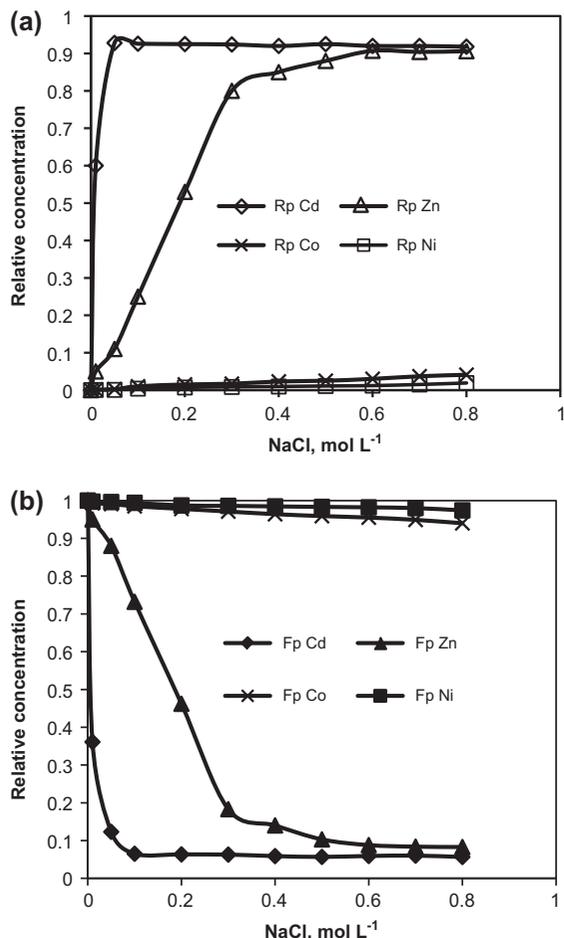


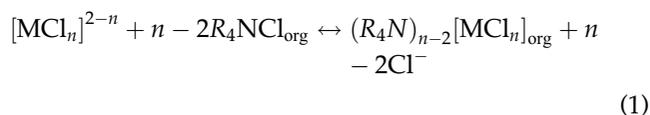
Fig. 2. Effect of sodium chloride concentration in the feed phase on the variation of metal ion concentration in the receiving (a) and feed (b) phases. Conditions: feed phase (Fp) 10 mL containing 25 mgL<sup>-1</sup> Cd(II), 30 mgL<sup>-1</sup> Zn (II), 10 mgL<sup>-1</sup> Co(II) and Ni(II) each, pH 7; membrane, 20 mL Aliquat 336 (0.05 mol L<sup>-1</sup>) in chloroform; receiving phase (Rp), 10 mL distilled water; time, 3 h;  $t = 25^\circ\text{C}$ .

consistent with the previously reported extraction of chloro complexes by quaternary ammonium salts from NaCl, i.e. the separation of Cd and Zn can be achieved by controlling the chloride concentration [8]. Moreover, the amount of Cl<sup>-</sup> required for Cd alone in present work is more than that used for cadmium and zinc in our previous work [22], where benzene was used as solvent. This is due to the larger logK for Cd in benzene (8.8) than in chloroform in present work (5.6) [15]. Hence, a 0.05 mol L<sup>-1</sup> concentration of sodium chloride was selected for further experiments.

### 3.2. Influence of feed solution pH

According to the following equation (Eq. (1)), the ion pair formation and extraction efficiency do not

directly depend upon the solution pH. However, dependency of metal–chloride complexes formation and/or the hydrolysis of the metal ions to pH provoke to study the influence of pH on transport efficiency. A set of experiments for the transport of cadmium ions (25 mgL<sup>-1</sup>) from sodium chloride solution (0.05 mol L<sup>-1</sup>) through a chloroform solution of Aliquat 336 (0.05 mol L<sup>-1</sup>) into distilled water as a function of pH was performed for 3 h. The results given as Fig. 3 confirms the expected behaviour, i.e. there was no metal concentration variation in the pH range of 1–7. However, the transport efficiency decreased gradually beyond pH 7 which might be due to the competition of chloride and hydroxide ions for metal ions (i.e. Cd(OH)<sup>+</sup> and/or Cd(OH)<sub>2</sub> formation) in alkaline pH, in the feed phase. According to (Eq. (1)), neither of these species can transfer into organic phase since the extraction is based on anion-exchange mechanism. Therefore, pH 6 was chosen as optimum value in further experiments, which is usually found for distilled water.



### 3.3. Effect of Aliquat 336 concentration in the membrane

In the transport process, carrier acts as a catalyst for the phase transfer by forming a lipophilic complex which diffuses into the membrane, and then releasing the analyte into the receiving phase. Therefore, its

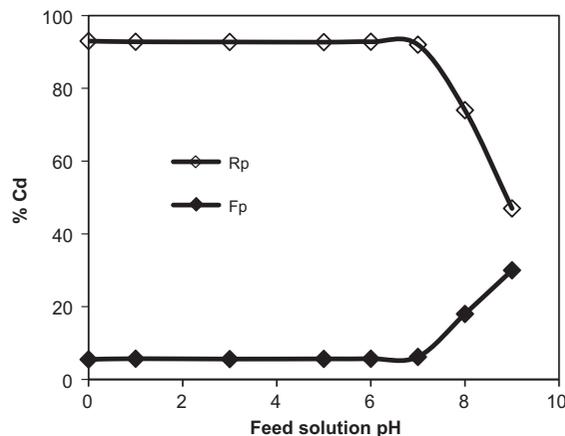


Fig. 3. Percentage of Cd(II) transport against pH of feed solution. Conditions: feed phase, 10 mL (Cd(II) 25 mgL<sup>-1</sup>), containing NaCl 0.05 mol L<sup>-1</sup>; membrane, 20 mL Aliquat 336 (0.05 M) in chloroform; receiving phase (Rp), 10 mL distilled water; time, 3 h;  $t = 25^\circ\text{C}$ .

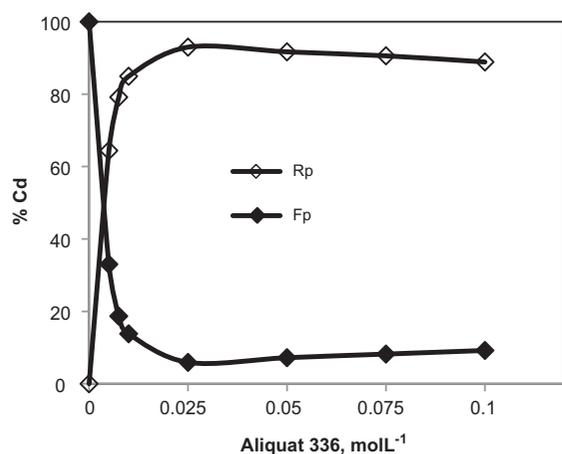


Fig. 4. Variation of Cd(II) percentage as a function of carrier concentration in the membrane phase. Conditions: feed phase (Fp), 10 mL (Cd(II) 25 mgL<sup>-1</sup>), containing NaCl 0.05 mol L<sup>-1</sup>, pH 6; membrane, 20 mL Aliquat 336 (0–0.1 mol L<sup>-1</sup>) in chloroform; receiving phase (Rp), 10 mL distilled water; time, 3 h;  $t = 25^{\circ}\text{C}$ .

concentration is an important factor affecting the transport efficiency. In order to investigate the influence of Aliquat 336 concentration on the transport efficiency, different concentrations of carrier were tested in the range of 0–0.1 mol L<sup>-1</sup>. According to Fig. 4, no mass transfer for metal ions occurs in absence of carrier, while the transport efficiency increased with increase in concentration up to 0.025 mol L<sup>-1</sup> carrier.

However, the extraction percentage decreased gradually at higher concentrations due to either an increase in liquid membrane viscosity, leading to mass transfer obstruction in the liquid membrane phase, as described in a previous report [23], polymerization or aggregation of aliquat 336. Hence, 0.025 mol L<sup>-1</sup> carrier was selected for further studies.

#### 3.4. Influence of Cd(II) concentration in feed solution

In order to evaluate the effect of initial Cd(II) concentration in the feed solution on the efficiency of its extraction, the transport experiments were performed by varying Cd(II) concentration in the range of 10–250 mgL<sup>-1</sup>, while maintaining the other parameters constant. Table 1 shows that the efficiency was decreased at high concentrations of cadmium. The decrease in

extraction efficiency at higher concentrations of Cd(II) may be because of increasing overall mass transfer resistance with higher Cd(II) concentration.

#### 3.5. Effect of organic diluent in membrane phase

The effect of organic diluent in membrane on the efficiency of process was investigated performing a series of experiments using carbon tetrachloride, chloroform, 1,2-dichloroethane and dichloromethane. The order of transport efficiency was found as: chloroform > carbon tetrachloride > 1,2-dichloroethane  $\approx$  dichloromethane. Hence, chloroform was chosen as suitable solvent for preparation of carrier solution. Although there is some effort to describe the diluents effect based on the polarity of the organic solvents, this interpretation is not applicable for the results obtained in the present work. Hence, there are other parameters affecting the obtained results.

#### 3.6. Selection of the receiving phase

Although distilled water was used in the preliminary experiments (being available, inert and cost effective), other solutions were also tested for the comparison purpose.

Therefore, the stripping ability of ammonia (2 mol L<sup>-1</sup>), ethylene diamine (en) (0.2 mol L<sup>-1</sup>), sulphuric acid (2 mol L<sup>-1</sup>), nitric acid (2 mol L<sup>-1</sup>) and EDTA (0.1 mol L<sup>-1</sup>) was examined. As can be seen in Fig. 5, the highest transport efficiency was observed for EDTA (96%) and then distilled water (93%). In contrast to our recent work [22], ammonia could not act as efficient stripping reagent since it mixes in membrane phase through hydrogen bonding leading to a decrease in its stripping capacity and finally, the receiving and membrane phases are mixed up. Water was selected as stripping phase due to its availability, non-toxicity, ease of handling, low cost of consumption and disposal.

#### 3.7. Influence of temperature

Although transport is known to be mainly controlled by a diffusion regime, the complex formation rate (kinetic regime) also may take part in transport of

Table 1  
Percentages of Cd(II) transport at different initial concentrations

Cd(II) initial concentration, mgL <sup>-1</sup>	10	50	100	150	200	250
Transport efficiency, %	93.6	92.0	91.7	90.3	88.6	85.0

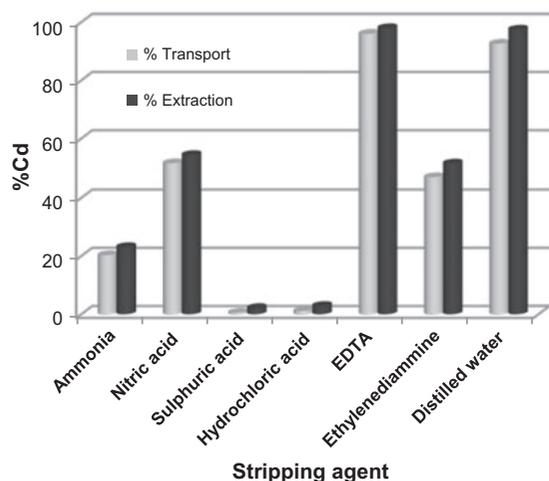


Fig. 5. Percentage of Cd(II) stripping versus different types of stripping agents under optimum conditions: feed phase (Fp), 10 mL (Cd(II) 25 mgL<sup>-1</sup>), containing NaCl 0.05 mol L<sup>-1</sup>, pH 6; membrane, 20 mL Aliquat 336 (0.025 mol L<sup>-1</sup>) in chloroform; time, 3 h; *t* = 25°C.

cations through a liquid membrane. Temperature has an important influence on the extraction process because it affects both the extraction time and the extraction efficiency. Increasing the temperature increase the diffusion coefficients of the target ions and also decreases the viscosity of the liquid membrane phase; it also may alter the reaction rate. Therefore, the influence of temperature on the efficiency of extraction and stripping was examined for temperatures in the range of 20–50°C. The results showed that the percentage of transport increases slightly with increasing temperature, as illustrated in Fig. 6. The variation in the percentage of transport was observed

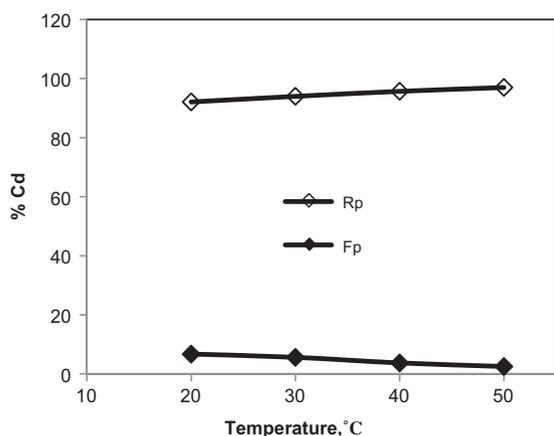


Fig. 6. Percentage of Cd(II) transport against temperature, with 20 mL Aliquat 336 (0.025 mol L<sup>-1</sup>) in chloroform; after 3 h; receiving phase (Rp), 10 mL distilled water.

as: from 92% at 20°C with relative error of 2% to approximately 97% at 50°C with relative error of 3.2%. Extraction efficiency tends to increase as the operating temperature increases.

However, the chloroform has a restricted operating temperature due to its boiling point ≈61°C. Hence, all the experiments were performed at 25°C.

### 3.8. Kinetics and Influence of operating time

Fig. 7 shows that an increase in time increased the amount of metal ions extracted from feed phase into the membrane phase as well as those stripped in the receiving phase.

Although the quantitative transport (95.5%) was obtained after 4 h, but 3 h was selected as optimum operating time since the rate of Zn<sup>2+</sup> co-transport was increased significantly beyond 3 h (result not shown). The kinetics of process was investigated by the model used by He and others [15,24], where the reduced concentrations were used.

$$R_f = \frac{C_f}{C_{f_0}} \quad (2)$$

$$R_m = \frac{C_m}{C_{f_0}} \quad (3)$$

$$R_r = \frac{C_r}{C_{f_0}} \quad (4)$$

Here  $C_f$ ,  $C_m$  and  $C_r$  denote the metal concentrations in the feed, membrane and receiving phases at

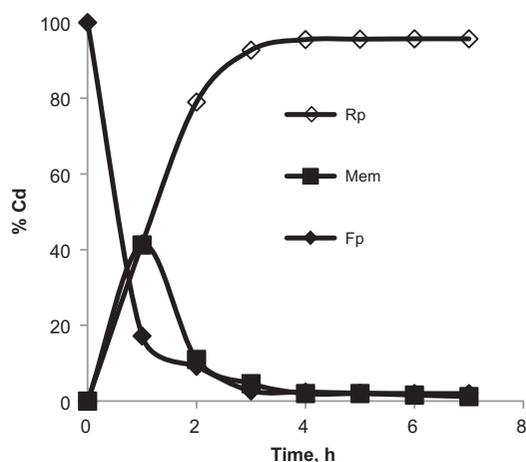


Fig. 7. Time dependency of Cd(II) concentration in the feed, receiving and membrane phases. Conditions: feed phase (Fp), 10 mL (Cd(II) 25 mgL<sup>-1</sup>), containing NaCl 0.05 mol L<sup>-1</sup>, pH 6; membrane, 20 mL Aliquat 336 (0.025 mol L<sup>-1</sup>) in chloroform; receiving phase (Rp), 10 mL distilled water; *t* = 25°C.

time  $>0$ , while the subscript “0” denotes the corresponding initial concentrations ( $t = 0$ ). Obviously,  $R_f + R_m + R_r = 1$ .

As can be seen from Fig. 7,  $R_f$  decreases mono-exponentially with time, and  $R_r$  follows a monotonically increasing sigmoidal curve while  $R_m$  shows a maximum. Therefore, it can be suggested that the metal ions transport obeys the kinetic laws of two consecutive irreversible first-order reactions according to the kinetic scheme [25],  $f \xrightarrow{k_1} m \xrightarrow{k_2} r$ . This kinetic scheme may be described by the (Eqs. (2)–(10)):

$$\frac{dR_f}{dt} = -k_1 R_f \quad (5)$$

$$\frac{dR_m}{dt} = k_1 R_f - k_2 R_m \quad (6)$$

$$\frac{dR_r}{dt} = k_2 R_m \quad (7)$$

where  $k_1$  and  $k_2$  are the rate constants in the feed–membrane and membrane–receiving interfaces, respectively. Integrating the above differential equations gives the reduced concentrations as following:

$$R_f = \exp(-k_1 t) \quad (8)$$

$$R_m = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (9)$$

$$R_r = 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (10)$$

It can be seen that  $R_f$  vs.  $t$  yields a decreasing mono-exponential curve where as the time variation of both  $R_m$  and  $R_r$  is bi-exponential.

The experimental results were analysed by non-linear curve fitting. The transport rate constants calculated by Eqs. (7)–(9) are as:  $k_1(1.19h^{-1})$ ,  $k_2(0.22h^{-1})$ , indicating that mass transfer at the feed–membrane interface is faster than that of the membrane–receiving interface.

### 3.9. Stability and reusability of the membrane

In order to examine the stability of the membrane phase, a single membrane was used for five replicate experiments while renewing the feed and receiving phases after each experiment. It was observed that the performance of the membrane did not change considerably; i.e. the transport efficiency of 93( $\pm 2$ )% at first experiment was changed to 90 ( $\pm 2.3$ )% at the fifth experiment. Hence, the membrane phase was considered stable up to five transport experiments.

### 3.10. Selectivity and application of the method

The selectivity of the proposed method towards cadmium ions was examined by performing the process for its equimolar binary mixtures with Co(II), Cu(II), Fe(III), Pb(II), Mn(II), Ni(II) and Zn(II) at the optimum conditions for Cd(II). The results given in Table 2 reveal the selectivity of the method towards Cd(II) transport with the yield of 92.4–93.3%. In order to access the applicability of the present method, it was applied for the recovery of cadmium from leach liquor of the zinc plant purification cake, spent Ni–Cd

Table 2  
Transport of cadmium ions from its mixtures with other coexisting metal ions at optimum condition

Binary mixtures	Initial concentration (mol L <sup>-1</sup> )	% Transport	
1	Cd <sup>+2</sup>	1 × 10 <sup>-4</sup>	93.00
	Zn <sup>+2</sup>	1 × 10 <sup>-4</sup>	11.00
2	Cd <sup>+2</sup>	1 × 10 <sup>-4</sup>	93.20
	Ni <sup>+2</sup>	1 × 10 <sup>-4</sup>	0.14
3	Cd <sup>+2</sup>	1 × 10 <sup>-4</sup>	92.83
	Co <sup>+2</sup>	1 × 10 <sup>-4</sup>	0.20
4	Cd <sup>+2</sup>	1 × 10 <sup>-4</sup>	92.40
	Cu <sup>+2</sup>	1 × 10 <sup>-4</sup>	1.30
5	Cd <sup>+2</sup>	1 × 10 <sup>-4</sup>	93.00
	Fe <sup>+3</sup>	1 × 10 <sup>-4</sup>	Not detected
6	Cd <sup>+2</sup>	1 × 10 <sup>-4</sup>	93.30
	Pb <sup>+2</sup>	1 × 10 <sup>-4</sup>	2.60
7	Cd <sup>+2</sup>	1 × 10 <sup>-4</sup>	92.94
	Mn <sup>+2</sup>	1 × 10 <sup>-4</sup>	0.10

Table 3  
Recovery of metal ions from real samples

Sample	Cation	Initial concentration (mgL <sup>-1</sup> )	Transport (%)
Ni–Cd cake	Cd <sup>2+</sup>	23.0 (±0.5) <sup>b</sup>	92.00
	Zn <sup>2+</sup>	45.0 (±0.3)	11.50
	Ni <sup>2+</sup>	8.0 (±0.4)	0.40
	Co <sup>2+</sup>	2.0 (±0.1)	0.50
Ni–Cd cell	Cd <sup>2+</sup>	67.4 (±0.4)	91.73
	Ni <sup>2+</sup>	134.9 (±0.1)	0.30
	Co <sup>2+</sup>	11.78 (±0.3)	0.70
Wastewater	Cd <sup>2+</sup>	8.0 (±0.6)	92.30
	Pb <sup>2+</sup>	61.0(±0.5)	2.70
	Zn <sup>2+</sup>	15.0 (±0.4)	10.6
	Ni <sup>2+</sup>	4.5 (±0.5)	0.20

<sup>a</sup>Samples prepared as Section 2.3.

<sup>b</sup>Values in the parentheses are standard deviations for triplicate analysis.

cells and wastewater with satisfactory results. The given results in Table 3 depict the effectiveness of the present method for recovery of cadmium from the real samples with high efficiency.

#### 4. Conclusions

The present work investigated the transport of Cd(II) from aqueous solutions and waste materials via bulk liquid membrane. The significant parameters were studied, i.e. the pH of the feed solution, Cd(II) concentration in the feed solution, the concentration of carrier, types of diluents, types of stripping agents, operating time and temperature. The highest percentages of Cd(II) transport (93%) were obtained with feed solution containing 0.05 mol L<sup>-1</sup> NaCl at pH 6, 0.025 mol L<sup>-1</sup> Aliquat 336 dissolved in chloroform as liquid membrane and distilled water as stripping agent. Therefore, cadmium ions can be effectively separated from coexisting metal ions. As pointed out in Section 3.10, the extraction of Cd(II) show higher selectivity over associated ions from chloride solution, this selectivity follows the tendency for each metal ion to form anionic chloro complexes. In contrast to our recent work [22], ammonia could not act as efficient stripping agent since it misses in membrane phase through hydrogen bonding and the phases are mixed up. Water was selected as stripping phase due to its availability, non-toxicity, ease of handling, low cost of consumption and disposal.

#### References

- [1] F. Habashi, Handbook of Extractive Metallurgy, Wiley-VCH, Weinheim, 1997.
- [2] W.C. Butterman and J. Plachy, Cadmium, mineral commodity profiles. U.S. Geological Survey, Open File Report, 2002.
- [3] J.C. Merrill, J.J.P. Morton, S. Soileau, Metals, in: A.W. Hayes (Ed.) Principles and Methods of Toxicology, fifth ed., Taylor and Francis, New York, NY, 2008, pp. 858–860.
- [4] C.D. Klassen, M.O. Amdur, J. Doull, Casarett and Doull's Toxicology: The Basic Science of Poisons, third ed., Macmillan, New York, NY, 1986.
- [5] M. Sadegh-Safarzadeh, M.S. Bafghi, D. Moradkhani, M. Ojaghi-Ilkhchi, A review on hydrometallurgical extraction and recovery of cadmium from various resources, Miner. Eng. 20 (2007) 211–220.
- [6] D.G.E. Kerfoot, R.D. Weir, The hydro and electrometallurgy of nickel and cobalt, Extractive Metall. Nickel Cobalt, Proc. Symp., 117th TMS Ann. Meet., Phoenix, AZ, 1988.
- [7] J. Rydberg, M. Cox, C. Musikas, G.R. Choppin, Solvent Extraction Principles and Practice, second ed., Marcel Dekker, New York, NY, 2004.
- [8] B. Wassink, D. Dreisinger, J. Howard, Solvent extraction separation of zinc and cadmium from nickel and cobalt using Aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms, Hydrometallurgy 57 (2000) 235–252.
- [9] Q. Jia, C.H. Zhan, D.Q. Li, C.J. Niu, Extraction of zinc (II) and cadmium (II) by using mixtures of primary amine N1293 and organophosphorus acids, Sep. Sci. Technol. 39 (2004) 1111–1123.
- [10] K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, Solvent extraction separation of Cd(II) and Zn(II) with the organophosphorus extractant D2EHPA and the aqueous nitrogen-donor ligand TPEN, Hydrometallurgy 70 (2003) 63–71.
- [11] K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, Extraction separation of Cd(II) and Zn(II) with Cyanex 301 and aqueous nitrogen-donor ligand TPEN, Sol. Extr. Ion Exch. 22 (2004) 203–218.
- [12] G. Haesbroeck, A. De Schepper and A. Van Peteghem, Solvent extraction of iron and zinc from concentrated CoCl<sub>2</sub> solutions at metallurgie hoboken-Overpelt,

- Extractive Metall. Nickel Cobalt, Proc. Symp., 117th TMS Ann. Meet., Phoenix, AZ, 1988.
- [13] A.M. Haji Shabani, S. Dadfarnia, F. Motavaselian, S.H. Ahmadi, Separation and preconcentration of cadmium ions using octadecyl silica membrane disks modified by methyltrioctylammonium chloride, *J. Hazard. Mater.*, 162 (2009) 373–377.
- [14] R.D. Noble, S.A. Stern (Eds.), *Membrane Separation Technology, Principles and Applications*, Elsevier, Amsterdam, 1994.
- [15] D. He, M. Ma, Z. Zhao, Transport of cadmium ions through a liquid membrane containing amine extractants as carriers, *J. Membr. Sci.* 169 (2000) 53–59.
- [16] L. Wang, R. Paimin, R.W. Cattrall, W. Shen, S.D. Kolev, The extraction of cadmium(II) and copper(II) from hydrochloric acid solutions using an Aliquat 336/PVC membrane, *J. Membr. Sci.* 176 (2000) 105–111.
- [17] F.J. Alguacil, M. Alonso, Transport of cadmium from a mixture of HCl and H<sub>3</sub>PO<sub>4</sub> using phosphine oxides (Cyanex 921 and Cyanex 923) as carriers: The influence of the membrane diluents (Exxsol D100 and Solvesso 100), *Hydrometallurgy* 74 (2004) 195–202.
- [18] S. Jafari, M.R. Yaftian, M. Parinejad, Facilitated transport of cadmium as anionic iodo-complexes through bulk liquid membrane containing hexadecyltrimethylammonium bromide, *Sep. Purif. Technol.* 70 (2009) 118–122.
- [19] R.S. Juang, H.C. Kao, W.H. Wu, Analysis of liquid membrane extraction of binary Zn(II) and Cd(II) from chloride media with Aliquat 336 based on thermodynamic equilibrium models, *J. Membr. Sci.* 228 (2004) 169–177.
- [20] R.A. Kumbasar, Transport of cadmium ions from zinc plant leach solutions through emulsion liquid membrane containing Aliquat 336 as carrier, *Sep. Purif. Technol.* 63 (2008) 592–599.
- [21] R.A. Kumbasar, Extraction of cadmium from solutions containing various heavy metal ions by Amberlite LA-2, *J. Ind. Eng. Chem.* 16 (2010) 207–213.
- [22] N. Dalali, H. Yavarizadeh, Y.K. Agrawal, Separation of zinc and cadmium from nickel and cobalt by facilitated transport through bulk liquid membrane using trioctyl methyl ammonium chloride as carrier, *J. Ind. Eng. Chem.* 18 (2012) 1001–1005.
- [23] C. Fontàs, C. Palet, V.Salvad, M. Hidalgo, A hollow fiber supported liquid membrane based on Aliquat 336 as a carrier for rhodium(III) transport and preconcentration, *J. Membr. Sci.*, 178 (2000) 131–139.
- [24] G. León, M.A. Guzmán, Facilitated transport of copper through bulk liquid membranes containing different carriers: compared kinetic study. *Desalination* 223 (2008) 330–336.
- [25] M. Szpakowska, O.B. Nagy, Membrane material effect on copper coupled transport through liquid membranes. *J. Membr. Sci.* 64 (1991) 129–143.